

# Redetermination of Mass Spectra of Deuteromethanes

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Mass spectra of the four deuteromethanes have been remeasured using samples of improved isotopic purity. The relative abundances of fragment ions involving loss of H or D atoms from the molecules  $\text{CH}_3\text{D}$ ,  $\text{CH}_2\text{D}_2$ , and  $\text{CHD}_3$  are not proportional to the a priori probabilities of removing H or D atoms but have been expressed in terms of the a priori probability times a weighting factor. The weighting factor for removing one H or D atom from these molecules can be roughly expressed as positive and negative powers of a single constant  $1.19 \pm 0.015$  and the same power law holds for the relative abundances of  $\text{H}^+$  and  $\text{D}^+$ . Weighting factors for removing two or more hydrogenic atoms are not consistent with this power law.

## 1. Introduction

A paper by this title by Dibeler and Mohler [1]<sup>1</sup> was published in 1950 and at about the same time a paper by Schissler, Thompson, and Turkevich [2] also included mass spectra of the four deuteromethanes. There are some discrepancies between the mass spectra reported in the two papers, and in both researches the isotopic purity of the molecules  $\text{CH}_2\text{D}_2$  and  $\text{CHD}_3$  left much to be desired. Deuteromethanes of much better isotopic purity have become available and it seemed worthwhile to repeat the measurements. It is important for analytical reasons to have reliable mass spectral patterns for the deuteromethanes. It is also of theoretical interest to know the relative probabilities of removing H and D atoms from the four deuteromethanes.

## 2. Experimental Details

The deuteromethanes were made by A. T. Morse of Merck and Co., Limited, Montreal, Canada. The isotopic analyses of  $\text{CH}_3\text{D}$ ,  $\text{CH}_2\text{D}_2$ , and  $\text{CHD}_3$  were made at an ionizing voltage below the appearance potential of  $\text{CH}_3^+$ . For methane the appearance potential of  $\text{CH}_4^+$  is 13.1 v and of  $\text{CH}_3^+$ , 14.4 v [3, 4]. This small difference makes the measurement rather insensitive and difficult. Tickner, Bryce, and Lossing [5] have pointed out that these measurements are also subject to small systematic errors because of small differences in the ionization potentials of the deuteromethanes. The results are given in table 1. These analyses are consistent with isotopic purities of 98 atom percent and for  $\text{CD}_4$  99 percent quoted by the supplier.

Mass spectra were recorded with a Consolidated Model 21-103 mass spectrometer under standard operating conditions. The recorded spectra were corrected for the contribution of the  $\text{C}^{13}$  isotope, for the isotopic impurities listed in table 1, and for a small amount of air (1.6% or less) probably introduced in handling the sample.

TABLE 1. Isotopic analysis of deuteromethanes

Monodeuteromethane.....	$\text{CH}_3\text{D}$ , 96.9%; $\text{CH}_4$ , 2.2%; $\text{CH}_2\text{D}_2$ , 0.9%.
Dideuteromethane.....	$\text{CH}_2\text{D}_2$ , 98.6%; $\text{CH}_3\text{D}$ , 1.3%; $\text{CHD}_3$ , 0.1%.
Trideuteromethane.....	$\text{CHD}_3$ , 97.1%; $\text{CH}_2\text{D}_2$ , 2.4%; $\text{CD}_4$ , 0.5%.
Tetra deuteromethane.....	$\text{CD}_4$ , 98.5%; $\text{CHD}_3$ , 1.5%.

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

## 3. Results

The corrected mass spectra are listed in table 2 and in the last row is given the sensitivity of the molecule ion peak in divisions per micron. In the spectra of  $\text{CH}_3\text{D}$  and  $\text{CH}_2\text{D}_2$  two ions contribute to some of the mass peaks. Thus both  $\text{CH}_2^+$  and  $\text{CD}^+$  contribute to the 14 peak and H<sub>2</sub> and D contribute to the 2 peak. In table 3 the abundance of ions heavier than mass number 12 has been computed on the assumption that the probability of removing one, two, or three hydrogenic atoms from the deuteromethane is proportional to the probability of removing H, 2H, and 3H from methane [1]. The ions  $\text{CH}^+$  and  $\text{CH}_2\text{D}^+$  from  $\text{CH}_3\text{D}$  and  $\text{CH}^+$ ,  $\text{CHD}^+$ , and  $\text{CHD}_2^+$  of  $\text{CH}_2\text{D}_2$  are observed, and with the above assumption the abundances of the other ions are derived.

TABLE 2. Mass spectra of deuteromethanes for 70 v electrons<sup>a</sup>

<i>m/e</i>	$\text{CH}_4$	$\text{CH}_3\text{D}$	$\text{CH}_2\text{D}_2$	$\text{CHD}_3$	$\text{CD}_4$
1.....	5.40	4.82	3.04	1.92	-----
2.....	0.42	0.95	1.47	2.64	3.86
3.....	-----	.13	0.18	0.16	-----
4.....	-----	-----	-----	.13	0.28
12.....	3.54	3.41	3.36	3.37	3.18
13.....	9.86	5.98	3.35	1.52	-----
14.....	19.4	10.5	7.64	7.89	7.33
15.....	89.3	23.7	11.3	5.84	-----
16.....	100	79.8	33.3	10.7	13.7
17.....	-----	100	65.7	51.9	-----
18.....	-----	-----	100	43.5	86.5
19.....	-----	-----	-----	100	-----
20.....	-----	-----	-----	-----	100
Sensitivity.....	58	57	57	57	57

<sup>a</sup> Relative intensities are corrected for the  $\text{C}^{13}$  isotope and for isotopic impurities listed in table 1.

The contribution of  $\text{H}_2^+$  to the mass 2 peak of  $\text{CH}_3\text{D}$  and  $\text{CH}_2\text{D}_2$  has been computed differently. It is assumed that the relative abundances of  $\text{H}_2^+$  and  $\text{HD}^+$  are in the same ratio as the probabilities of removing 2H and H+D from the molecules. There should be a  $\text{D}_2^+$  ion from  $\text{CH}_2\text{D}_2$ , which is not observed, but the predicted intensity is 0.014 percent, which is at the threshold for observation. Computed abundances for  $\text{H}_2$  and  $\text{D}_2$  in table 3 are enclosed in parentheses.

Table 3 includes under P the a priori probabilities for the distribution of H and D in the fragment

ions. The observed abundance ratios are quite different from the a priori probability ratios and the abundance of each fragment ion can be expressed in terms of the a priori probability times a weighting factor. Table 4 gives the weighting factors for each ion with the notation that  $a_1$  is the factor for removing one H atom,  $a_2$  for two atoms, etc., and  $b$  is the factor for D atoms. The table includes for comparison the published values for these weighting factors.

TABLE 3. Ion abundances in methanes and a priori probabilities

Ion	CH <sub>4</sub>	CH <sub>3</sub> D	P <sup>a</sup>	CH <sub>2</sub> D <sub>2</sub>	P <sup>a</sup>	CHD <sub>3</sub>	P <sup>a</sup>	CD <sub>4</sub>
H-----	5.40	4.82	$\frac{3}{4}$	3.04	$\frac{1}{2}$	1.92	$\frac{1}{4}$	-----
D-----	-----	0.69	$\frac{1}{2}$	1.35	$\frac{1}{2}$	2.64	$\frac{3}{4}$	3.86
H <sub>2</sub> -----	0.42	(.26)	$\frac{1}{2}$	(0.12)	$\frac{1}{6}$	-----	-----	-----
HD-----	-----	.13	$\frac{1}{2}$	.18	$\frac{2}{3}$	0.16	$\frac{1}{2}$	-----
D <sub>2</sub> -----	-----	-----	-----	(.014)	$\frac{1}{6}$	.13	$\frac{1}{2}$	0.28
C-----	3.54	3.41	-----	3.36	$\frac{1}{2}$	3.37	-----	3.18
CH-----	9.86	5.98	$\frac{3}{4}$	3.35	$\frac{1}{2}$	1.52	$\frac{1}{4}$	-----
CD-----	-----	4.02	$\frac{1}{4}$	6.73	$\frac{1}{2}$	7.89	$\frac{3}{4}$	7.33
CH <sub>2</sub> -----	19.4	6.48	$\frac{1}{2}$	0.91	$\frac{1}{6}$	-----	-----	-----
CHD-----	-----	13.2	$\frac{1}{2}$	11.3	$\frac{2}{3}$	5.84	$\frac{1}{2}$	-----
CD <sub>2</sub> -----	-----	-----	-----	7.63	$\frac{1}{6}$	10.7	$\frac{1}{2}$	13.7
CH <sub>3</sub> -----	89.3	10.6	$\frac{1}{4}$	-----	-----	-----	-----	-----
CH <sub>2</sub> D-----	-----	79.8	$\frac{3}{4}$	25.7	$\frac{1}{2}$	51.9	$\frac{3}{4}$	-----
CHD <sub>2</sub> -----	-----	-----	-----	65.7	$\frac{1}{2}$	43.5	$\frac{1}{4}$	86.5
CD <sub>3</sub> -----	-----	-----	-----	-----	-----	-----	-----	-----

<sup>a</sup> P is a priori probability for distribution of H and D in fragment ions.

TABLE 4. Isotope weighting factors for deuteromethanes

Ion	CH <sub>3</sub> D	CH <sub>2</sub> D <sub>2</sub>	CHD <sub>3</sub>
H-----	$a_1=1.17$	$a_1=1.39=1.18^2$	$a_1=1.68=1.19^3$
D-----	$b_1=0.50=1.19^{-4}$	$b_1=0.616=1.17^{-3}$	$b_1=0.77=1.14^{-2}$
CH-----	$(a_2b_1=0.798=1.12^{-2})$	$(a_1b_2=0.665=1.12^{-4})$	$(b_3=0.65=1.05^{-3})$
CD-----	$a_3=1.61=1.17^3$	$(a_2b_1=1.336)$	$(a_1b_2=1.12)$
CH <sub>2</sub> -----	$a_1b_1=0.66=1.16^{-3}$	$(b_2=0.275=1.24^{-6})$	-----
CHD-----	$a_2=1.34=1.16^2$	$a_1b_1=0.86=1.16^{-1}$	$(b_2=0.706)$
CD <sub>2</sub> -----	-----	$a_2=2.30=1.23^4$	$(a_1b_1=1.29)$
CH <sub>3</sub> -----	$b_1=0.47=1.21^{-4}$	-----	-----
CH <sub>2</sub> D-----	$a_1=1.18$	$b_1=0.562=1.21^{-3}$	-----
CHD <sub>2</sub> -----	-----	$a_1=1.44=1.20^2$	$b_1=0.726=1.18^{-2}$
CD <sub>3</sub> -----	-----	-----	$a_1=1.82=1.22^3$
Ref. 1-----	$(b_1=0.45=1.22^{-4})$	$b_1=0.57=1.21^{-3}$	$(b_1=0.87)$
Ref. 2-----	$a_1=1.18$	$a_1=1.43=1.20^2$	$(a_1=1.41)$
	$(b_1=0.55=1.16^{-4})$	$b_1=0.65=1.14^{-3}$	$b_1=0.76=1.15^{-2}$
	$a_1=1.23$	$a_1=1.48=1.22^2$	$a_1=1.80=1.22^3$

## 4. Discussion

In a paper by Dibeler, Mohler, and de Hemptinne on the deuterioethylenes [6] it was shown that all the "weighting factors" could be expressed as positive and negative integral powers of one constant. In the present notation, the constant was  $a_1$  of C<sub>2</sub>H<sub>3</sub>D = 1.10. In table 4 many of the "weighting factors" have been expressed as powers of numbers, using the power law that applied for ethylene. Results show that this power law does not account for all weighting factors in the methanes. It is a rough approximation for some but not all of the weighting factors. Thus  $a_1$  for CH<sub>3</sub>D, CH<sub>2</sub>D<sub>2</sub>, and CHD<sub>3</sub> is 1.18, 1.20<sup>2</sup>, and 1.22<sup>3</sup>, whereas  $b_1$  is 1.21<sup>-4</sup>, 1.21<sup>-3</sup>, and 1.18<sup>-2</sup>. For weighting factors of H<sup>+</sup> and D<sup>+</sup>,  $a_1$  is 1.17, 1.18<sup>2</sup>, and 1.19<sup>3</sup> whereas  $b_1$  is 1.19<sup>-4</sup>,

1.17<sup>-3</sup>, and 1.14<sup>-2</sup>. Weighting factors for removing two or three atoms are in some cases roughly consistent with the power law, but in general the agreement is poor. Values enclosed in parentheses do not fit, and values for C<sup>+</sup> and for all of the CD<sub>4</sub> spectrum do not vary in the manner found for C<sub>2</sub><sup>+</sup> of the ethylenes and for the C<sub>2</sub>D<sub>4</sub> spectrum.

It is of interest that in the deuteromethanes the weighting factors for H<sup>+</sup> and D<sup>+</sup> are nearly the same as for removing H and D from the molecule ions. An apparent exception is  $b_1$  for D<sup>+</sup> of CHD<sub>3</sub> but this may be an experimental error. Another set of measurements gave  $b_1=0.73=1.17^{-2}$ . The sensitivities at mass 1 and mass 2 are not expected to be quite the same and are subject to some variation whenever focusing adjustments are changed. The roots of the weighting factors for removing H or D from the molecule ions and for abundance of H<sup>+</sup> and D<sup>+</sup> have a mean value of  $1.19 \pm 0.01$ .

Table 4 includes published values of  $a_1$  and  $b_1$  for CH<sub>3</sub>D, CH<sub>2</sub>D<sub>2</sub>, and CHD<sub>3</sub>. The values derived in this research are in satisfactory agreement with published values of Dibeler and Mohler [1] for the first two molecules, but the published data for CHD<sub>3</sub> are evidently in error. Values given by Schissler, Thompson, and Turkevich [2] are roughly consistent with the present values for all three molecules.

The mass spectra reported in table 2 should be more reliable than the previously published values because of the good isotopic purity of the molecules. The fact that weighting factors are not all related by a power law can not be explained as experimental uncertainty. Some of the mass spectra have been remeasured and recomputed several times and results have been consistent.

The mean value of the roots of the weighting factors for deuteromethanes 1.19 can be compared with the constants 1.10 for the ethylenes and 1.13 for acetylenes [5]. Schissler, Thompson, and Turkevich [2] report a value of 1.09 for monodeuteroethane. In monodeutero benzene and monodeutero naphthalene it was found that the factor is nearly unity [7]. There is no obvious explanation for weighting factors that differ much from unity as is the case for the deuteromethanes.

## 5. References

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